

ORGANIC-INORGANIC PEROVSKITES

Lower threshold for nanowire lasers

Hybrid perovskite is introduced as a new material for nanowire lasers. One-dimensional nanostructures of these perovskites can be optically pumped to lase with tunable wavelength at relatively low threshold, which marks a step towards their use in integrated photonics.

Anthony Fu and Peidong Yang

Semiconductor nanowires are excellent candidates for the realization of miniaturized lasers; in fact, their faceted structure naturally behaves as an optical cavity in which light can resonate, and the gain medium they are made of provides the optical amplification required to trigger lasing action¹. Bottom-up fabrication approaches have unlocked the synthesis of nanowires based on a broad family of materials that are inaccessible through conventional top-down techniques, especially for materials with complex compositions. Writing in *Nature Materials*, Haiming Zhu and colleagues now show² that hybrid organic–inorganic metal halide perovskites, which have recently transformed photovoltaic research³, are also an outstanding member of this materials family.

The low-temperature synthesis of organic–inorganic metal halide perovskite nanowires using solution-processed methods is nontrivial. In fact, this material is known to be generally unstable in water and in many polar organic solvents. In addition, the traditional vapour–liquid–solid process for the synthesis of semiconductor nanowires requires a metal droplet to initiate the one-dimensional crystal growth⁴, but it is unlikely that a metal catalyst can be found for this complex organic–inorganic metal halide perovskite. An alternative, catalyst-free approach has been proposed for the synthesis of semiconductor nanowires, in which screw dislocations (linear crystallographic defects) in seed particles are used to initiate the nanowire growth⁴. The strain induced in the crystallographic structure by these defects promotes fast one-dimensional growth of the crystal in a helical trajectory, in a direction along the axis of the screw dislocation.

Zhu and colleagues were able to synthesize, at temperatures as low as 80 °C, perovskite nanowires following this catalyst-free route. They deposited a polycrystalline film of lead acetate onto a glass substrate and dipped it into a solution of isopropyl alcohol and $\text{CH}_3\text{NH}_3\text{X}$, where X = Cl, Br, I, or a halide mixture. According to the growth

mechanism suggested by the researchers, at this stage part of the lead acetate layer reacts with the solution and is converted into a thin film of $\text{CH}_3\text{NH}_3\text{PbX}_3$ with many dislocations. This initial perovskite film is a diffusion barrier that prevents further rapid reaction between the solution and the lead acetate remaining underneath the film. The slow dissolution of Pb from the unreacted lead acetate produces an intermediate precursor, PbI_4^{2-} , which promotes the growth of crystalline nanowires driven by the dislocations in the perovskite seed layer.

Through various characterization techniques, the researchers observed that each nanowire is a single crystal with

smooth facets, which makes these structures efficient nanoscale optical cavities. This result is particularly intriguing considering that high temperatures are generally needed to grow inorganic crystals with sufficient quality for lasers and solar cells, and that traditional inorganic semiconductor nanowire lasers are generally grown at temperatures greater than 400 °C in a typical gas phase deposition process^{1,4}. These perovskites defy conventional expectations by combining the low-processing temperatures of organic materials with the extended translational symmetry of inorganic crystals, which is favourable for charge transport.

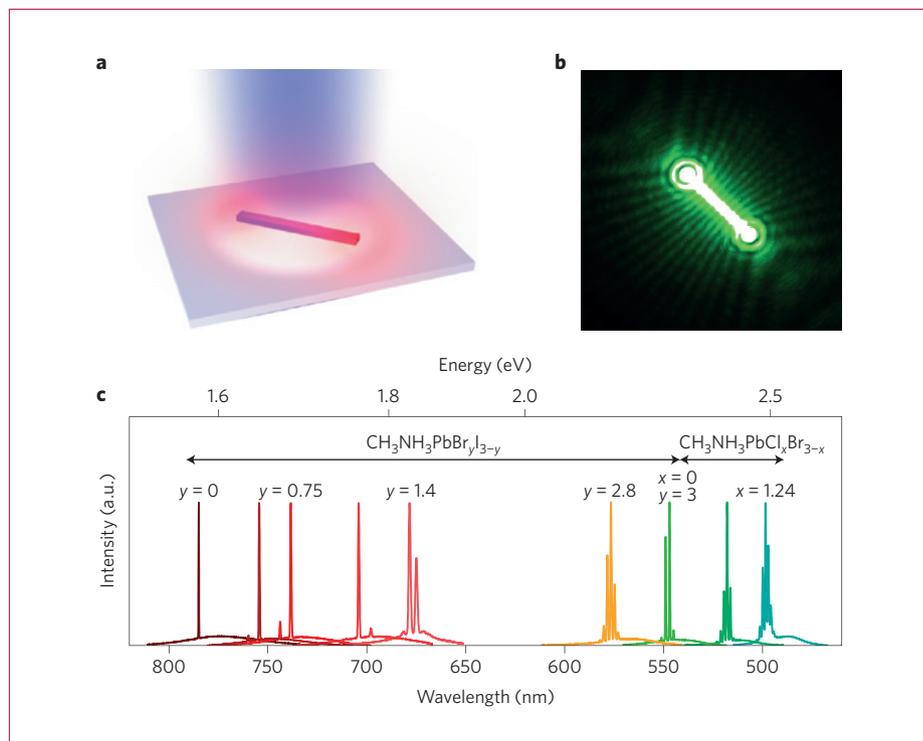


Figure 1 | Lasing in hybrid organic–inorganic metal halide perovskite nanowires. **a**, Illustration of an optically pumped perovskite nanowire on a Si substrate with 300-nm-thick SiO_2 . **b**, Optical image of a 13.6- μm -long $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanowire showing lasing emission. **c**, Lasing spectra of various alloy compositions of mixed lead halide perovskite nanowires demonstrating widely tunable laser emission at room temperature. Figure reproduced from ref. 2, Nature Publishing Group.

The nanowires showed an extremely high light-emitting efficiency, higher than 87% for the iodide samples. Importantly, the researchers observed lasing emission at optical stimulation as low as 220 nJ cm^{-2} , with tunability of the lasing wavelength across the visible spectrum obtained by modifying the material composition (Fig. 1). Lasing from films⁵ or platelets⁶ of hybrid organic–inorganic perovskites has already been reported, yet the performance of these first prototypes was not optimal, possibly as a result of the limited crystalline quality of the materials used. The exceptional low lasing threshold of the perovskite nanowire lasers of Zhu and co-workers, lower than that of any other semiconductor nanowire to date, is a direct proof of the significant reduction of structural defects obtained with the growth approach used; in fact, optical losses due to scattering or to imperfect reflections of the mirror end-facets are strongly attenuated.

A complete understanding of the growth mechanism of these nanowires will require

further investigation. Although imaging by means of transmission electron microscopy would provide direct confirmation of the screw-dislocation-driven growth, such analysis has proved challenging because perovskite materials are unstable under the electron-beam irradiation conditions required by this technique. Hence, alternative approaches will have to be used to validate the one-dimensional growth model proposed by these researchers. In addition, a complete rate equation model describing the photophysical processes taking place in these perovskite materials may help to improve our understanding of the threshold behaviour. Last, the demonstration of electrically injected lasing will require the development of fabrication strategies and device architectures that minimize the detrimental increase of optical losses, which are due to the deposition of metallic contacts on the cavity.

It is interesting that these ionic perovskite materials seemingly have optical properties that are comparable to classic

covalent semiconductors such as gallium arsenide. However, this ionic character also contributes to their sensitivity to air and moisture, and is likely to limit their potential application in advanced photonic circuits if this stability issue is not addressed. Yet the exceptional performance reported by Zhu and colleagues has already put hybrid organic–inorganic perovskites at the forefront of laser research. □

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References

1. Yan, R., Gargas, D. & Yang, P. *Nature Photon.* **3**, 569–576 (2009).
2. Zhu, H. *et al.* *Nature Mater.* **14**, 636–642 (2015).
3. Green, M. A., Ho-Baillie, A. & Snaith, H. J. *Nature Photon.* **8**, 506–514 (2014).
4. Dasgupta, N. P. *et al.* *Adv. Mater.* **26**, 2137–2184 (2014).
5. Deschler, F. *et al.* *J. Phys. Chem. Lett.* **5**, 1421–1426 (2014).
6. Zhang, Q., Ha, S. T., Liu, X., Sum, T. C. & Xiong, Q. *Nano Lett.* **14**, 5995–6001 (2014).

IMPLANTED MATERIALS

Larger is stealthier

Implanted spheres with a diameter larger than 1.5 mm escape fibrotic responses, thereby extending the survival time of the encapsulated therapeutic cells.

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The immune system recognizes implanted materials as foreign, triggering an orchestrated series of sequential events that are collectively known as the foreign body reaction (FBR)¹. The outcome of a FBR is the complete elimination of the implanted material via degradation or, alternatively, via the generation of a fibrotic capsule that shields the material from the body. Because of an ageing population, there is an increasing demand for tissue implants and implanted delivery systems, which calls for increased efforts to better understand the FBR. Harnessing the FBR is of considerable importance to successfully design biomaterials that attenuate fibrotic responses (so as to improve the half-life of the implant)^{1,2} or that allow for a precise control of their degradation rates (and hence the formation of new tissue). Writing in *Nature Materials*, Daniel Anderson and colleagues demonstrate with a series of straightforward experiments a surprisingly simple solution to circumvent the unwanted

fibrotic encapsulation of implanted spheres³. They show that the size of implanted spheres determines the extent of the body's fibrotic response, with bigger spheres triggering a lower FBR (Fig. 1).

Implanted spheres can be used for drug- or cell-delivery applications, for example, to host cells that secrete clinically relevant drugs (such as insulin). Yet, the injection of microspheres in tissues normally results in inflammation, a process that involves the recruitment of macrophages and fibroblasts as well as the macrophage-triggered activation of the latter. This results in myofibroblasts capable of producing a fibrotic capsule of densely packed collagen around the implant that hinders the release of drugs, thus impairing the implant's function.

Anderson and co-authors found that spheres with a small diameter (0.5 mm or less) implanted in mice, rats or monkeys elicited a severe fibrotic response, whereas larger, 1.5-mm spheres hardly induced capsule formation. Also, they observed that

such a size effect persisted across a diverse range of materials, including alginate, stainless steel, glass, polycaprolactone and polystyrene, and that it was not restricted to a specific tissue (the authors injected the spheres subcutaneously or in the intraperitoneal space). Moreover, the size effect was restricted to spherical shapes, as increasing the implant size without taking the spherical geometry into consideration provoked fibrosis or rejection.

The mechanism behind such an apparently universal phenomenon is not clear, however. Anderson and colleagues observed minimal cell numbers (neutrophils, macrophages and myofibroblasts) on the surface of the larger spheres as well as little activity in the movement of these cells from the surrounding tissue to the larger implanted spheres (these experiments involved real-time tracking of fluorescent macrophages⁴ in genetically modified mice). The opposite occurred for the smaller, 0.5-mm-sized spheres. They also observed differences in